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STORAGE

INVESTIGATIONS ON INDIAN OPIUM

No. 3

STUDIES IN THE MECONIC ACID CONTENT OF INDIAN OPIUM

BY

HAROLD E. ANNETT, D.Sc. (Lond.), F.I.C., M.S.E.A.C., Etc

Agricultural Chemist, on special duty, Cawnpore

AND

MATHURA NATH BOSE, M.A. (Cal.)



AGRICULTURAL RESEARCH INSTITUTE, PUSA

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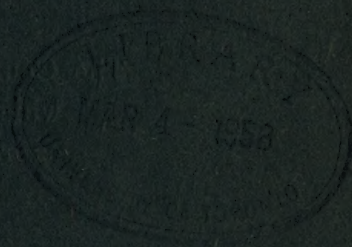
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CHEMICAL SERIES

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INVESTIGATIONS ON INDIAN OPIUM

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STUDIES IN THE MECONIC ACID CONTENT OF INDIAN OPIUM.

BY

HAROLD E. ANNETT, D.Sc.(Lond.), F.I.C., M.S.E.A.C., ETC.,
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MATHURA NATH BOSE, M.A. (Cal.).

(Received for publication on 21st March, 1922.)

CERTAIN organic acids such as malic, citric, succinic, oxalic and tannic acids appear to be of common occurrence in many species of plants. Quinic acid occurs in the bark of cinchonas and in coffee roots and has recently been found by Tanret¹ in *Cedrus Libani*. Lactic acid has been reported to occur in the sap of the vine² and in opium.³ Fluckiger and Hanbury,⁴ however, state that it is probably not an original constituent of poppy juice. We agree with this view and also suggest that lactic acid in the sap of the vine has been produced by fermentation having no connection with the life processes of the plant. Meconic acid has so far only been met with in opium, the produce of the opium poppy. Since meconic acid is strictly peculiar to opium it would appear that a study of the amount of this acid in opium samples produced under different experimental conditions might lead to an increased knowledge of the physiology of the opium poppy plant.

METHOD OF ANALYSIS.

The methods available appeared to us unsatisfactory and we adopted the following method of estimating meconic acid in opium. It is being fully described in the *Analyst*.

¹ *Comptes rend.*, 1921, **172**, 234.

² Thorpe. *Dict. App. Chem.*, III, p. 221.

³ T. & H. Smith. *Pharm. Jour.* (ii), **7**, 50.

⁴ *Pharmacographia*.

Five gram. of opium are rubbed up carefully with water in a mortar and transferred to a stoppered flask using 50 c.c. of water in all. The flask is well shaken and allowed to stand overnight. The liquid is then filtered and a measured quantity, *e.g.*, 40 or 45 c.c. of the filtrate, is taken for meconic acid estimation.

Six c.c. of 50 per cent. CaCl_2 solution are added, the liquid shaken and allowed to stand 24 hours. Any attempt to partially neutralize the opium solution before addition of the CaCl_2 always results in the production of meconic acid contaminated with colouring matters. The precipitate is then filtered off in a Hirsch funnel and washed with water till the washings are colourless and consists almost entirely of calcium meconate and calcium sulphate. It is almost perfectly white. The precipitate is transferred to a small beaker by the aid of 15 c.c. of 1.25 N hydrochloric acid, the filter paper being removed. The beaker is then heated on the water bath until the precipitate has completely dissolved. The liquid is then allowed to stand in a cool place for 24 hours. Meconic acid separates in white crystalline scales in highly pure condition. It is filtered in a Hirsch funnel, being removed completely from the beaker by means of the mother liquor and then washed twice with $\frac{1}{2}$ c.c. distilled water, dried between filter paper and then in a dessicator over H_2SO_4 for 3 hours and weighed as $\text{C}_7\text{H}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$.

The amounts of water used for extraction of the opium and of hydrochloric acid used for decomposition of the calcium meconate precipitate were decided on after a series of experiments with pure meconic acid.

The result is then calculated by adding 0.0213 gram. to the weight of meconic acid found to correct for the solubility of meconic acid in 15 c.c. of 1.25 N HCl. We then multiply the figure obtained by a factor depending on the amount of the aliquot portion of the opium solution taken for analysis. If this were 45 c.c. we multiply by 50/45. We multiply the figure obtained by 10/9, since we have found that roughly about 10 per cent. of the meconic acid is unprecipitated by the calcium chloride. The following example illustrates the method of calculation. In a certain analysis we took 5 gram. of opium and extracted with 50 c.c. water. We took 44 c.c. of the filtrate for precipitation with CaCl_2 and obtained 0.2744 gram. meconic acid. The calculation is as follows:—

$(0.2744 + 0.0213) \times \frac{50}{44} \times \frac{10}{9}$ = corrected weight of meconic acid from 50 c.c. of solution or 5 gram. opium.

$\therefore$ in 100 gram. opium we get $(0.2744 + 0.0213) \times \frac{50}{44} \times \frac{10}{9} \times \frac{100}{5}$
= 7.47 per cent. meconic acid in opium.

THE MECONIC ACID CONTENT OF OPIUM.

In our previous memoirs¹ in this series we have examined the effect of various factors both environmental and non-environmental on the morphine content of Indian Opium. The experimental samples made use of for that work were available for the work described in the present paper. There was, however, no need for a complete investigation of the meconic acid content of these samples, for it was soon discovered that the meconic acid content varies almost directly with the total alkaloid content of the opium. Factors modifying the alkaloidal content therefore necessarily modify meconic acid extent.

Our investigations on the alkaloidal content of opium have established the fact that when an opium capsule is lanced for opium on a number of successive occasions at one or more days' intervals the morphine content of the opium rapidly diminishes in the product of each succeeding lancing.²

We find also that the meconic acid content of the opium of a series of successive lancings of a capsule falls off in a manner somewhat similar to the way in which the morphine content diminishes. The following table sets out the results of the analyses of the opium of a number of successive lancings of poppy capsules as regards the morphine and meconic acid content.

Composition of opium in percentage on dry matter.

Series No.					No. OF LANCING			
					1st	2nd	3rd	4th
I	(a) morphine	..	..		13.3	9.5	6.0	4.3
	(b) meconic acid	..	..		9.7	7.0	5.8	5.8
II	(a) morphine	..	..		13.3	10.2	5.0	1.2
	(b) meconic acid	..	..		9.6	8.0	5.0	3.7
III	(a) morphine	..	..		13.8	11.4	7.9	..
	(b) meconic acid	..	..		9.7	8.1	5.6	..
IV	(a) morphine	..	..		13.6	9.2	5.9	..
	(b) meconic acid	..	..		8.1	6.1	4.2	

It will be seen that in the first three lancings at least there is a fairly rapid successive diminution in meconic acid content. The fall is not so marked as it is in the case of morphine, yet it is distinct.

Opium of second lancings always contains less meconic acid than opium of first lancings and the third lancings contain less still. In the fourth

¹ Mem. of the Dept. of Agri. in India, Vol. VI, Nos. 1 and 2.

² Mem. of the Dept. of Agri. in India, Vol. VI, No. 1.

lancings, however, the meconic acid content does not appear notably less than in the third lancings.

A number of other samples of opium taken from our collection containing widely varying percentages of morphine were next submitted to analysis for meconic acid content. The following results were obtained, the figures being arranged in order of the highest morphine content opium downwards.

Composition of dry matter of opium.

No. of sample	Morphine per cent.	Meconic acid per cent.
372	18.44	9.79
373	18.14	9.90
1077-87	17.00	9.17
43	16.35	10.55
49	15.97	9.29
55	15.25	9.43
61	15.22	9.70
108	14.18	7.08
37	14.12	9.58
67	14.11	9.40
44 (1)	13.80	9.72
270 (1)	13.62	8.06
19	13.51	8.50
144	13.29	9.57
386	13.26	9.73
25	13.18	8.53
31	13.04	8.47
44 (2)	11.40	8.06
147	10.20	7.99
387	9.50	7.02
270 (2)	9.16	6.12
44 (3)	7.90	5.56
388	6.01	5.77
270 (3)	5.92	4.25
148	5.05	4.99
389	4.35	5.83
620 H	1.87	3.56
596 H	1.74	4.04
150	1.18	3.75
Hill sample	0.00	4.67

The figures show points of some interest. In the first place opiums of high morphine content always contain a high percentage of meconic acid. Roughly speaking opiums containing 16 per cent. morphine contain 10 per cent. meconic acid. We have examined opiums containing less than 2 per cent. morphine but these still contain 3 to 4 per cent. meconic acid. A sample of opium showing no morphine by the British Pharmacopœia process yet still showed 4.67 per cent. meconic acid. In the case of high morphine content opiums, however, we never find a low content of meconic acid. Thus an

opium containing 13 per cent. morphine is always found to contain at least 8.5 per cent. meconic acid.*

The foregoing results thus showed that though samples of opium poor in morphine also contained small amounts of meconic acid and vice versâ yet the relation between morphine and meconic acid content was not direct. It was accordingly resolved to make a more complete analysis of a series of opium samples. Among our collections we have many sets, each representing the opium of successive lancings of the same capsules. We selected four of these sets at random, each set consisting of three successive lancings of the same capsules. Thus there were 12 samples in all. Each sample was analysed for morphine, codeine, narcotine and papaverine, meconic acid and soluble sulphate. For the morphine estimations we made use of the method of the British Pharmacopœia (1914). In the case of codeine we used our own method¹ or rather a slight improvement of it which is shortly to be published. For narcotine and papaverine we used a new method which we are communicating to the *Analyst*. This latter method is very accurate and estimates narcotine and papaverine together.

Our results are summarized in the following table.

Sample No.	Description of sample				PERCENTAGE ON DRY MATTER OF OPIUM					
					Morphine	Codeine	Narcotine + Papaverine	Total alkaloids	Water soluble sulphate as SO ₄	Calculated meconic acid required for alkaloids estimated
170	1st lancings	1917-18	..	11.54	2.85	3.81	23.20	2.40	9.41	9.09
171	2nd do.	1917-18	..	7.47	2.75	7.81	18.03	2.87	6.90	6.92
172	3rd do.	1917-18	..	4.04	2.29	6.90	13.23	3.26	5.32	4.92
320	1st lancings	1918-19	..	12.07	3.05	11.77	26.89	2.08	11.10	10.37
322	2nd do.	1918-19	..	9.84	3.06	11.53	24.43	2.56	9.54	9.30
324	3rd do.	1918-19	..	6.11	3.64	9.71	19.46	3.43	7.35	7.30
301	1st lancings	1919-20	..	12.09	3.29	12.00	27.38	2.38	11.07	10.63
302	2nd do.	1919-20	..	8.80	3.27	10.08	22.15	2.96	8.01	8.54
303	3rd do.	1919-20	..	4.68	3.16	8.60	16.44	3.35	6.34	6.17
386	1st lancings	1920-21	..	13.10	3.21	10.90	27.21	2.62	10.63	10.61
387	2nd do.	1920-21	..	9.69	2.92	8.07	20.68	3.28	8.10	8.09
388	3rd do.	1920-21	..	6.76	2.81	6.90	16.47	3.97	6.88	6.36

* We found one exception, viz., No. 108, which showed only 7.08 per cent. meconic acid whereas it contained 14.18 per cent. morphine.

¹ *The Analyst*, September 1920.

A column has been added to the table showing the amount of meconic acid theoretically required to combine with the morphine, codeine, narcotine and papaverine actually found. Two molecules of the alkaloid require one molecule of $C_7H_4O_7 \cdot 3H_2O$.

The table brings out the striking fact that the meconic acid content of opium is almost exactly what would be required to ensure that the alkaloids are present solely as meconates. Thus the amount of meconic acid found agrees fairly closely in practically every case with the amount calculated as being necessary to convert all the alkaloids to meconates. As a rule the actual amount of meconic acid found appears to be slightly greater than the calculated amount. In this connection it must be remembered that there are a number of other rarer alkaloids present in opium whose total amount is about 1 per cent. and which would require roughly 0.25 per cent. of meconic acid to enable them to exist as meconates. Any slight irregularity between the actual meconic acid found and the calculated amounts might easily be due to inaccuracies in analytical methods. Thus we do not claim absolute accuracy for our method of estimating meconic acid and the British Pharmacopœia method of estimating morphine is after all only approximate.

The agreement in so many cases between the actual amounts of meconic acid found and the amounts calculated as being necessary for the alkaloids to be present as meconates is so remarkable that one must be forced to the conclusion that the alkaloids occur in the latex solely as meconates. The acid reaction of opium is easily accounted for owing to the weakly basic nature of narcotine and papaverine, the meconic acid equivalent to them reacting as free acid. This relationship between the total alkaloid content and the meconic acid content of the latex has one interesting bearing on our former work. We have shown that the morphine content diminishes in the latex of each successive lancing. We have been unable to find that the decrease in morphine content is accompanied by any increase in the content of any other alkaloid. The relationship above referred to is confirmatory evidence that the decrease in morphine content of the lancing is not counterbalanced by an increase in any other alkaloid so far not estimated.

The above table also shows that the sulphate content increases in each successive lancing and thus bears almost an inverse relationship to the alkaloids content. It is unlikely, therefore, that the alkaloids occur as sulphate.

These facts are interesting as showing the form in which the alkaloids occur in the latex. Dott¹ states that morphine occurs in opium half combined as

¹Watt's Dict. of Chem., III, 437.

meconate and half as sulphate but the foregoing results show that this is not the case.

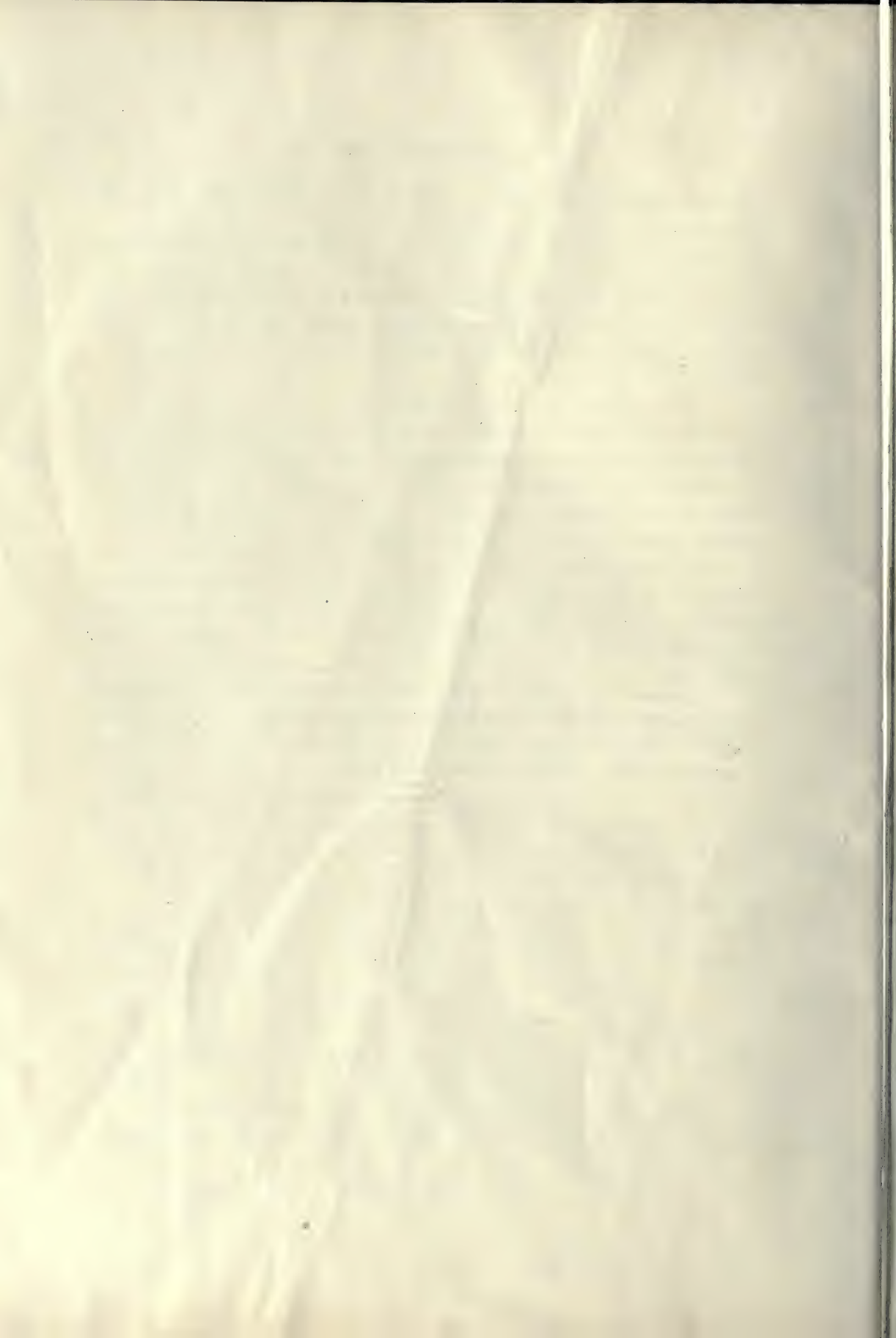
It will be convenient to refer here to the fact that the total ash constituents of the latex vary inversely with the total alkaloid content. Thus the total ash content of each successive lancing increases whereas the alkaloidal content rapidly diminishes. The ash constituents of opium will, however, form the subject of a separate memoir in this series.

CONCLUSIONS.

1. The meconic acid content of opium varies directly as the total alkaloid content and the acid appears to be present in approximately sufficient amounts to enable all the alkaloids to be combined as meconates. It would thus seem that the physiological process whereby alkaloids are produced in the opium poppy produces meconic acid in equivalent amount to the alkaloids.

2. The soluble sulphate content of the latex increases as the alkaloidal content diminishes. From the table on p. 219, it can be calculated that in the early lancements there is insufficient sulphate to completely combine with the total alkaloids but in the later lancements there is more than sufficient for this purpose.

It appears most likely, however, that the sulphate is present in a mineral form and that the alkaloids are present as meconates only, the acid reaction of opium being due to the dissociation of the meconates of narcotine and papaverine, which alkaloids are so weakly basic.



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